

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-054133

(43)Date of publication of application : 26.02.1999

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(51)Int.Cl.

H01M 6/16

H01M 10/40

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(21)Application number : 09-210870

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(22)Date of filing : 05.08.1997

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## (54) NONAQUEOUS ELECTROLYTE BATTERY

### (57)Abstract:

PROBLEM TO BE SOLVED: To provide an electrolyte which restrains self-discharge when a battery is preserved and whose preserving characteristic is improved by including a specific quantity of dioxolane in an organic solvent containing oxygen acid ester.

SOLUTION: At least one kind of oxygen acid ester selected from a group of phosphoric ester, boric acid ester and titanilic acid ester is included in an organic solvent containing dioxolane  $\geq 10$  wt.%. When a nonaqueous electrolyte composed of this organic solvent and a solute is used, the oxygen acid ester reacts with lithium in the presence of dioxolane to form a good quality coating film on a negative electrode. Since this coating film restrains direct contact of lithium with the solvent, the decomposition of the nonaqueous electrolyte is restrained. Trimethyl phosphate is thought to easily form an optimal coating film on the negative electrode or to be easily attracted on the negative electrode in the oxygen acid ester, and a self-discharge rate is further restrained.

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### LEGAL STATUS

[Date of request for examination]

24.05.2001

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

3439084

[Date of registration]

13.06.2003

[Number of appeal against examiner's decision of

rejection]

[Date of requesting appeal against examiner's  
decision of rejection]

[Date of extinction of right]

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CLAIMS

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[Claim(s)]

[Claim 1] A nonaqueous electrolyte cell characterized by for said dioxolane containing 10% of the weight or more to said organic solvent, and said organic solvent containing oxygen acid ester in a nonaqueous electrolyte cell equipped with a nonaqueous electrolyte which consists of a positive electrode, a negative electrode which consists of a possible negative-electrode material of occlusion bleedoff of a lithium or a lithium, an organic solvent containing dioxolane, and a solute.

[Claim 2] A nonaqueous electrolyte cell according to claim 1 characterized by being at least one sort chosen from a group which said oxygen acid ester becomes from phosphoric ester, the ester of boric acid, and titanate.

[Claim 3] A nonaqueous electrolyte cell according to claim 2 by which said phosphoric ester is characterized by being trimethyl phosphate.

[Claim 4] A nonaqueous electrolyte cell according to claim 2 by which said titanate is characterized by being titanic-acid tetra-isopropyl.

[Claim 5] A nonaqueous electrolyte cell according to claim 2 by which said ester of boric acid is characterized by being trimethyl borate.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to amelioration of the conservation property of the nonaqueous electrolyte cell which used the lithium as a negative-electrode active material, i.e., a lithium cell.

[0002]

[Description of the Prior Art] The lithium cell using a lithium as a negative-electrode active material attracts attention as a high energy density cell, and active research is done.

[0003] Generally by this seed cell, independence, such as ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, a sulfolane, 1, 2-dimethoxyethane, a tetrahydrofuran, and dioxolane, two components, or 3 component mixture is used as a solvent which constitutes a nonaqueous electrolyte. And  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiASF}_6$  and  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ , and  $\text{LiCF}_3(\text{CF}_2)_3\text{SO}_3$  grades can be enumerated as a solute dissolved into this.

[0004] By the way, two components containing dioxolane independence or dioxolane or a 3 component mixed solvent, and the nonaqueous electrolyte that consists of a solute have the problem to which the cell capacity after conservation falls in order to cause a reaction with the chemical negative electrode which uses an organic solvent and a lithium as an active material. Therefore, it has been an important technical problem in utilization of this seed cell to control the self-discharge at the time of conservation.

[0005] By the way, raising the property of a cell is proposed by using for JP,60-91565,A the nonaqueous electrolyte which contains dioxolane in a solvent. However, if dioxolane is used for \*\* et al. and a solvent, in order to cause a reaction with the chemical negative electrode which uses a lithium as an active material, there is a problem that the cell capacity after conservation falls.

[0006] Then, although the method of adding a pyridine is in the electrolytic solution in order to raise a conservation property as indicated by JP,49-108525,A, also in this method, in the case of the cell using the organic solvent containing dioxolane, sufficient property is not acquired but there is room of amelioration.

[0007]

[Problem(s) to be Solved by the Invention] This invention controls the self-discharge at the time of saving this seed cell, and proposes the outstanding nonaqueous electrolyte which raises a conservation property.

[0008]

[Means for Solving the Problem] This invention is characterized by for said dioxolane containing 10% of the weight or more to said organic solvent, and said organic solvent containing oxygen acid ester in a nonaqueous electrolyte cell equipped with a nonaqueous electrolyte which consists of a positive electrode, a negative electrode which consists of a possible negative-electrode material of occlusion bleedoff of a lithium or a lithium, an organic solvent containing dioxolane, and a solute.

[0009] It will be the basis of existence of dioxolane of the amount of specification, this oxygen acid ester will react with a lithium, and this reason will form a good coat on a negative electrode, if a nonaqueous electrolyte which added oxygen acid ester is used for an organic solvent which contained dioxolane 10% of the weight or more. Since this coat controls direct contact to a lithium and a solvent, it is considered to control decomposition of a nonaqueous electrolyte which makes contact to a lithium and the electrolytic solution \*\*. Thus, it becomes possible to raise the conservation property of a cell.

[0010] In addition, as the above-mentioned oxygen acid ester, trimethyl phosphate  $[(\text{CH}_3\text{O})_3\text{PO}]$ , titaniumbutylate  $[(\text{C}_4\text{H}_9\text{O})_4\text{Ti}]$ , trimethyl borate  $[(\text{CH}_3\text{O})_3\text{B}]$ , phosphoric-acid triethyl  $[(\text{C}_2\text{H}_5\text{O})_3\text{PO}]$ , titanilic-acid tetra-isopropyl  $[(\text{C}_3\text{H}_7\text{O})_4\text{Ti}]$ , and boric-acid triethyl  $[(\text{C}_2\text{H}_5\text{O})_3\text{B}]$  can be illustrated.

[0011] And since it is thought that it is easy to adsorb on a negative electrode and control of a rate of self-discharge is much more attained also in said oxygen acid ester or trimethyl phosphate tends to form coat optimal on a negative electrode, it is desirable.

[0012] As a solute of this seed cell, although  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiASF}_6$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  and  $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ ,  $\text{LiCF}_3(\text{CF}_2)_3\text{SO}_3$ , and  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$  grade can be used, it is not limited to this.

[0013] It is possible to consider as mixture of three or more components which added ethylene carbonate, propylene carbonate, butylene carbonate, vinylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, a sulfolane, and a tetrahydrofuran to what contained dioxolane 10% of the weight or more, and added oxygen acid ester as an organic solvent of this seed cell.

[0014] Although a metallic oxide containing manganese, cobalt, nickel, vanadium, and at least one sort of niobium can be used as a positive electrode of this seed cell, it is not limited to this.

[0015] As a negative electrode of this seed cell, what uses a lithium ion as occlusion and matter which can be emitted, and uses a metal lithium as an electrode material electrochemically is illustrated. Considering a lithium ion as occlusion and matter which can be emitted, lithium alloys, such as carbon materials, such as a graphite, corks, and an organic substance baking object, and a lithium-aluminum alloy, a lithium-Magnesium alloy, a lithium-indium alloy, a lithium-tin alloy, a lithium-thallium alloy, a lithium-lead alloy, and a lithium-bismuth alloy, are illustrated electrochemically.

[0016]

[Embodiment of the Invention] Below, it explains in full detail per example of this invention.

(Experiment 1) Half section drawing of the flat form nonaqueous electrolyte cell as one example of this invention is shown in drawing 1. The negative electrode 1 which consists of a lithium metal is stuck to the inner surface of the negative-electrode charge collector 2 by pressure, and has fixed this negative-electrode charge collector 2 on the inner base of the negative-electrode can 3 of the shape of a cross section KO character which consists of ferritic stainless steel (SUS430). It is fixed to the interior of the insulating packing 4 made from polypropylene, the peripheral edge of the above-mentioned negative-electrode can 3 becomes the periphery of the insulating packing 4 from stainless steel, and the positive-electrode can 5 which makes the shape of a cross section KO character to an opposite direction is being fixed in the above-mentioned negative-electrode can 3. The positive-electrode charge collector 6 is being fixed to the inner base of this positive-electrode can 5, and the positive electrode 7 is being fixed to the inner surface of this positive-electrode charge collector 6. Between this positive electrode 7 and said negative electrode 1, the separator 8 with which impregnation of the nonaqueous electrolyte which is the main point of this invention was carried out is infixed.

[0017] By the way, the manganese dioxide heat-treated at the temperature of 400 degrees C is used for said positive electrode 7 as an active material. Said heat treatment can be changed in a 350-430-degree C temperature requirement. This manganese dioxide, the carbon powder as an electric conduction agent, and the fluororesin powder as a binder are mixed by the weight ratio of 85:10:5, respectively. Next, after carrying out pressing of this mixture, desiccation processing was carried out at 300 degrees C, and the positive electrode 7 was produced. It can set up and this desiccation processing can be changed in a 250-350-degree C temperature requirement.

[0018] On the other hand, said negative electrode 1 is produced by piercing a lithium rolled plate in a predetermined size.

[0019] And a trifluoro methansulfonic acid lithium is dissolved in the mixed organic solvent (they are five kinds, 10:0, 9:1, 5:5, 1:9, and 0:10, at a weight ratio) of trimethyl phosphate  $[(\text{CH}_3\text{O})_3\text{PO}]$  and dioxolane (DOXL) which is oxygen acid ester as the electrolytic solution at a rate of one mol/l. as a solute, and a nonaqueous electrolyte is obtained. The cell A1 with an outer diameter [ of 20.0mm ] and a thickness of 2.5mm - A5 were produced using this nonaqueous electrolyte.

(Experiment 2) It replaced with the trimethyl phosphate used in said experiment 1, and a cell B1 - B5 were similarly produced except having used trimethyl borate  $[(\text{CH}_3\text{O})_3\text{B}]$  as oxygen acid ester.

(Experiment 3) It replaced with the trimethyl phosphate used in said experiment 1, and cells C1-C5 were similarly produced except having used titanate-acid tetra-isopropyl  $[(\text{C}_3\text{H}_7\text{O})_4\text{Ti}]$  as oxygen acid ester.

[0020] The conservation property of each cell was compared using these cells A1 - A5, B1 - B5, and C1-C5. After this experiment condition produced each cell and saved it for two months at 60 degrees C, it made the cell discharge actually and the rate of self-discharge (%) was provided by it as a percentage to the capacity before saving that difference as compared with the capacity before conservation. This result is shown in a table 1.

[0021]

[A table 1]

溶媒混合重量比 酸素酸トリメチル : D O X L		1 0 : 0	9 : 1	5 : 5	1 : 9	0 : 1 0
添 加 剤	リン酸トリメチル	A1 12.0	A2 7.0	A3 4.1	A4 7.1	A5 12.0
	ホウ酸トリメチル	B1 12.0	B2 7.2	B3 4.3	B4 7.1	B5 12.0
	チタン酸テトラ イソプロピル	C1 12.0	C2 7.1	C3 4.2	C4 7.0	C5 12.0

[0022] As for this invention cell A2 - A4, B-2 - B4, and C2-C4, this table 1 shows that the rate of self-discharge is small, lowering of the cell capacity at the time of conservation is suppressed, and self-discharge is controlled as compared with the comparison cell A1, A5, B1, B5, and C1 and C5. In addition, as for cell A5, cell B5, and a cell C5, oxygen acid TORIMECHIRU is not added.

[0023] In addition, although the addition of trimethyl phosphate, trimethyl borate, and titanitic-acid tetra-isopropyl is changed as oxygen acid ester in experiments 1-3, the same inclination is observed even if it is a cell using other additives, phosphoric-acid triethyl, boric-acid triethyl, and titaniumbutylate.

[0024] although trifluoro methansulfonic acid lithium  $\text{LiCF}_3\text{SO}_3$  was shown in each above-mentioned example as a solute dissolved in a nonaqueous electrolyte --  $\text{LiPF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ ,  $\text{LiC}(\text{CF}_3\text{SO}_3)_3$ , and  $\text{LiCF}_3(\text{CF}_2)_3$  -- it cannot be overemphasized that  $\text{SO}_3$  and  $\text{LiAsF}_6$  can be used. Moreover, although the mixed solvent of propylene carbonate and dioxolane was illustrated as an organic solvent, it is possible to use the mixture which contained dioxolane 10% of the weight or more, and added butylene carbonate, vinylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, and a tetrahydrofuran here.

[0025]

[Effect of the Invention] As mentioned above, the conservation property of this seed cell can be raised by adding at least one sort in the oxygen acid ester which is an organic solvent, and its derivative to the nonaqueous electrolyte which contained dioxolane 10% of the weight or more to the organic solvent. And for example, as said oxygen acid ester, trimethyl phosphate, trimethyl borate, and titanitic-acid tetra-isopropyl can be illustrated. Also in this, especially trimethyl phosphate is suitable. Consequently, the conservation property of a nonaqueous electrolyte cell can be improved notably, and that industrial value is very large.

[Translation done.]